McKELLOGG

The Composition of Boiler Compounds

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THE COMPOSITION OF BOILER COMPOUNDS

BY

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A. B. Oberlin College, 1914

THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

CARL STONE McKELLOGG

ENTITLED THE COMPOSITION OF BOILER COMPOUNDS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Arts

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CHAPTER I.

BOILER PRACTICE.

Very few boiler users have a good supply of soft water available. The waters which they are forced to use may foam, corrode, or deposit scale within the boiler. To correct these evils, certain mixtures, called boiler compounds, are used.

A boiler compound is anything which is added to the water within the boiler for the purpose of preventing scale formation, foaming or corrosion of the boiler plates or tubes. It does not apply to softening materials used outside the boiler to soften the feed water, but only to those substances whose action takes place within the shell.

A certain air of mystery has surrounded the composition of these compounds and little of importance has been written concerning them. We have aimed to review what has been published, to devise a suitable scheme of analysis, and to show something concerning their composition by the analyses of a number of typical compounds.

The ideal water is a water free from turbidity, organic matter, dissolved gases, and salts of calcium, magnesium, iron and aluminium, and containing a moderate amount of mineral matter in solution. Distilled waters are to be avoided since such waters, due to their natural tendency to absorb anything

with which they come in contact, are very corrosive.[*]

Ideal waters are rarely met with in nature. It becomes necessary then to use waters which may contain a large amount of foaming, corrosive or scale forming elements. Examples of such poor waters are the alkaline waters of the southwest, which cause excessive foaming under certain conditions, the sea water used in the boilers of battleships, whose corrosive action has been the subject of much study[**]; and the deep well waters of Illinois whose scale forming activities are familiar to boiler users of this vicinity.

Foaming results in wet steam which lowers the efficiency of the boiler. It may also change the level in the water guage so that, due to insufficient water in the boiler, overheating may result. Foaming depends on several factors. The concentration of alkaline salts, the amount of suspended matter, the amount of steam space, and the demands made upon the engine all contribute to the tendency of a water to foam. The limit of alkaline salt concentration in locomotive boilers is fixed at about 860 parts per million. This may be much larger in the case of stationary

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[*] W. M. Booth. Boiler Waters and their Treatment. Chemical Engineer, I. 1904, 282.

[**] W. W. Christie. Boiler Waters, 1906, 70.

boilers where load and speed are constant, and the steam space is larger. Unusual demands upon a boiler, such as starting and climbing grades in the case of a locomotive, greatly increase the tendency to foam. Suspended matter and other conditions may cause foaming where the concentration of alkali is no more than 300 parts per million. Professor Parr* thinks that, if the water could be entirely free from finely divided particles, the tendency to foam would be nearly, if not completely, removed.

Corrosion tends to weaken the boiler and ultimately results in a leaky shell and tubes, which must be discarded. In most cases it is an oxidization, ferric oxides being formed according to the reactions:

$$4Fe + 3O_2 = 2Fe_2O_3.$$

$$3Fe + 2O_2 = Fe_3O_4.$$

Dissolved gases and air reaching the inside of the boiler without process of solution are the most destructive agents.**

Magnesium chloride and sulphate act as oxidizing agents by decomposing the water according to the reactions:***

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*Boiler Waters. Water Survey Series, IV. 1908, 60.

**The Chemical Engineer. IX. 1909, 43.

***W. W. Christie. Boiler Waters. 1906, 79.

$$HOH = H + OH.$$

$$Fe + 2\ OH = Fe(OH)_2.$$

$$FE(OH)_2 + MgCl_2 = Mg(OH)_2 + FeCl_2.$$

Water, if very low in mineral content, will dissolve some of the iron directly. Such a condition may be found in some condenser systems. Unless some raw water from the feed pipe is constantly added, the water which enters the boiler will be nearly mineral free, and, as a result of this, will have a decided tendency to corrode. Electrolytic action, set up by the presence of copper or zinc, and chemical action, following the use of tannic acid as a boiler compound, may also corrode the shell and tubes.

Scale formation is the most common source of boiler troubles. Scale formation is objectionable for three reasons: first, because it lowers the efficiency of the boiler by preventing transmission of heat to the boiler; second, because it may prevent the heat applied from being radiated fast enough, thus causing overheating of the plates; and third, because it necessitates shutting down at intervals to clean out the scale.

The most important salts in scale formation are the sulphates and carbonates of calcium and magnesium, and the hydroxides of iron and aluminium. These form the "insoluble" minerals in water. The "soluble" minerals are the chlorides, nitrates and sulphates of the alkalis and the chlorides and nitrates of calcium and magnesium. Of course, by double decomposi-

tion, the latter salts may be changed to insoluble forms. The salts of the alkalis are all more soluble in hot water than in cold, and are precipitated only by saturation or the action of another salt.*

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*F. W. Mohlman. The Relation of the Mineral Content of Boiler Waters to that of the Scale Formed. Thesis for B.S. Illinois 1912, 4.

Steam generation is a continuous process, fresh water being supplied to the boiler as the water evaporated leaves it. The water which leaves the boiler is in a high state of purity as compared with that which enters. This constant excess of mineral matter results in a growing concentration of impurities. When this concentration reaches the limit of solubility, as determined by the pressure and the concentration of the various salts, precipitation begins. The character and hardness of this deposit varies with the composition of the mineral matter dissolved. The carbonates of calcium and magnesium tend to form a soft scale or sludge, which may be blown out. The sulphates of calcium and magnesium and the hydroxides of iron and aluminium tend to form a hard scale. Varying proportions of these scale forming materials will result in a scale which has a hardness intermediate between the two extremes.**

**W. C. Marti. Treatment of Water With Boiler Compounds. Water Survey Series VIII. 1911, 59.

Considerable experimental work has been done upon the effect of scale on heat transmission. Some of the earlier investigators of this subject were of the opinion that scale lowered the efficiency of the boiler as much as one fourth. More recent experiments have shown this figure to be too high. A series of tests carried on by E. C. Schmidt and J. M. Snodgrass showed these results.*

"1. Considering scale of ordinary thickness, say of thickness varying up to one-eighth of an inch, the loss of heat transmission due to scale may vary in individual cases from insignificant amounts up to 10 or 12 per cent.

2. The loss increases somewhat with the thickness of the scale.

3. The mechanical structure of the scale is of as much or more importance than the thickness in producing this loss.

4. Chemical composition, except in as far as it effects the structure of the scale, has no direct effect on the heat transmitting qualities."

It has already been shown that the amount of mineral matter in the boiler is constantly being increased. This must ultimately result in the deposition of some material since none

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*Effect of Scale on the Transmission of Heat Through Locomotive Boiler Tubes. Bulletin #11, Illinois Engineering Experiment Station. 1907.

of the salts commonly found in the boiler are soluble in all proportions. Boiler cleaning thus becomes a necessity and the question of the most efficient way of cleaning arises.

Two methods of treatment are in use at present, previous softening, including removal of temporary hardness by feed water heating, and treatment within the boiler. The most desirable of these, from the viewpoint of efficiency, is previous softening. The comparatively high cost of installing and operating such a plant is almost the only reason why such plants are not in use with all boilers where a hard water must be used. In spite of this drawback, a number of the railroads and large manufactories of the United States have installed such plants and regard them as paying investments.* By this method of treatment, the greater part of the calcium and magnesium is removed before the water enters the boiler, thus doing away with the salts which form hard scale. This obviates the necessity of cleaning scale from the boiler or feed water heater and at the same time keeps the concentration of total salts, and to a lesser extent of alkaline salts, since none are added to soften, lower, thus diminishing the danger of foaming.

Most of the softening plants in use today are modifications of the Porter-Clark process. This depends upon the removal of carbonic acid, calcium carbonate, and magnesium carbonate by

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*W. W. Christie. Boiler Waters. 1906, 191.

precipitating with lime, and the removal of calcium and magnesium sulphates by precipitation with soda ash. The reactions involved are:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + 2\ H_2O.$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2\ H_2O.$$

$$MgCO_3 + Ca(OH)_2 = CaCO_3 + Mg(OH)_2.$$

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3.$$

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2\ NaCl.$$

Feed water heating is not primarily a water softening process but is usually installed as a fuel-saving device. Its softening properties depend upon the decreasing solubilities of the scale forming minerals. As these salts are less soluble in hot water than in cold, precipitation takes place in the feed-water heater instead of in the boiler. If feed-water heaters be built with this fact in mind, the scale may be deposited here and handled to advantage. The feed-water heater does not remove all of the scale-forming minerals but it may lower their concentration to such a point that they are harmless.

The method now in use where the scale-forming minerals are dealt with within the boiler consists of treatment with materials which tend to make the precipitation take place as a soft sludge which may be blown out at intervals. A great number of things, ranging from potatoes to electricity, and explained by a number of theories have been proposed and tried with varying

success. The probable explanation for the action of each substance, in so far as it is understood, will be given later under the classification of boiler compounds along with some discussion of its economic value and its effect on the boiler shell and tubes.

Classification of Boiler Compounds.

The general scheme of classification used in one proposed by Mr. Albert A. Cary.* He divides the materials as follows:

1. Those that attack the scale producing material chemically.
    a. Organic matter including salts of organic acids.
    b. Inorganic matter.
2. Those acting mechanically upon the precipitated crystals of scale forming matter soon after they are formed.
3. Those acting both mechanically and as a solvent.

Organic Matter.

Tannins and their salts predominate among the organic substances which have a chemical action. This is introduced into the boiler in a number of different forms; as sawdust, blocks of wood, bark and extract of bark or wood. The principal sources of the tannins are oak, chestnut, hemlock, shumac, turmerac, catechu, logwood and mahogany. The sodium salt is commonly prepared by

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*American Mechinist. XXII. 1902, 1154.

making the acid solution slightly alkaline with soda ash.* Often the spent liquors from tanneries are used. The liquors from present day tanning practice contain no more than .5 per cent of tannin. Their efficiency then as a boiler compound cannot be very high.

Tannins, and salts of tannins, undergo a number of reactions in the boiler. The most common one, and the one in which we are most interested, is the double decomposition with a calcium or magnesium salt, as;

$$2\ C_7H_6O_5 + CaCO_3 = Ca(C_7H_5O_5)_2 + H_2CO_3.$$

$$2\ NaC_7H_5O_5 + MgSO_4 = Mg(C_7H_5O_5)_2 + Na_2SO_4.$$

Besides this there are changes from one tannin to another which take place on boiling. Not all of these are fully worked out but several are understood. Ordinary tannin (digallic acid) or its alkaline salt is transformed to gallic acid according to the reaction:

$$C_{14}H_{10}O_9 + H_2O = 2\ C_7H_6O_5$$

If this boiling is prolonged a further change takes place to pyrogallic acid according to the reaction;

$$C_7H_6O_5 = C_6H_6O_3 + CO_2$$

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*H. de la Coux. L'eau dans l'industrie. 1900, 65.

These reactions are aided by the presence of alkali.

A second series of reactions takes place if the tannin contains quercitron, an oak product.

$$\underset{\text{(Quercitron)}}{C_{33}H_{30}O_{17}} + H_2O = \underset{\text{(Quercetine)}}{C_{27}H_{18}O_{12}} + \underset{\text{(isodulcite)}}{C_6H_{14}O_6}.$$

$$\underset{\text{(Quercetine)}}{C_{27}H_{18}O_{12}} + 2\ H_2O = 2\ \underset{\text{(Phloroglucinol)}}{C_6H_6O_3} + \underset{\text{(Quercitic acid)}}{C_{15}H_{10}O_7} + O.$$

This decomposition, like that of tannic acid, is favored by the presence of alkali. The quercitic acid reacts with the scale forming minerals in the usual way, so that the precipitate formed in the boiler consists of a combination of the digallate, gallate, pyrogallate and quercitate of calcium and magnesium.*

The use of tannin and sodium tannate as a boiler compound has been investigated and the fact that it greatly increases corrosion brought out.** W. M. Booth in an article on boiler compounds says, "I can strenuously condemn tannic acid, and of the use of its salts I am fearful."† That it removes scale is an assured fact, that

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*H. de la Coux. L'eau dans l'industrie. 1900, 62.

**W. C. Marti. Treatment of Water with Boiler Compounds. University of Illinois Bulletin, State Water Survey Series No. 8, 70.

† Boiler Waters and their Treatment. Chemical Engineer, I,1904,367.

it removes iron with the scale is also assured, as tannic acid corrodes an iron surface rapidly. In spite of this corrosion it is very commonly used and is regarded as satisfactory by many users.

The oxalates of sodium and potassium* have also been used as boiler compounds. Their action removes the calcium salts but has little effect on the magnesium. The reactions involved are:

$$2\ Na_2C_2O_4 + Ca(HCO_3)_2 + CaSO_4 = 2\ CaC_2O_4 + Na_2CO_3 + Na_2SO_4.$$

$$Na_2CO_3 + Ca(HCO_3)_2 = CaCO_3 + 2\ NaHCO_3.$$

The action obtained here is a very desirable one, the calcium being precipitated in a convenient form without increasing corrosion. The high price of the $Na_2C_2O_4$ makes the salt impractical for general use.

This by no means covers all the organic substances which have a chemical action in the boiler. Many other organic acids and salts of organic acids are present in the various woods and barks which are used as a source of boiler compounds. The action of all of these depends upon the formation of a floculent precipitate which may be easily blown from the boiler. The action and value of these are similar to the action and value of tannin.

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*H. de la Coux. Leau dans l'industrie. 1900, 72.

Inorganic Matter.

Foremost in use among inorganic salts is sodium carbonate. It is equally effective when used in its crude form (soda ash) or in the purified form. As soda ash, it can be purchased at a very cheap rate (about 1 cent per pound). It does not corrode but, when used in excess, causes or increases foaming. This tendency to cause foaming is the chief drawback to its use as a boiler compound. The reactions involved are:*

$Ca(HCO_3)_2 + 2\ Na_2CO_3 = Na_4H_2(CO_3)_3 + CaCO_3.$

$Na_4H_2(CO_3)_3 = 2\ NaHCO_3 + Na_2CO_3.$

$2\ NaHCO_3 + NaCO_3 = 2\ Na_2CO_3 + H_2O + CO_2.$

$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$

$CaCl_2 + Na_2CO_3 = CaCO_3 + 2\ NaCl.$

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*H. de la Coux. L'eau dans l'industrie. 1900, 67.

Similar reactions take place in the case of magnesium salts. Properly added this is one of the most valuable boiler compounds obtainable.

Sodium hydroxide, as a boiler compound, must be used with extreme caution because of its decided tendency to corrode. In excess it is injurious to fittings, gaskets, valves, etc.**

**W. M. Booth. Boiler waters and their treatment. Chemical Engineer, I, 1904, 367.

It must be added in small amounts and not allowed to be in excess. The reactions involved are as follows:*

$$Ca(HCO_3)_2 + 2\ NaOH = CaCO_3 + Na_2CO_3 + 2\ H_2O.$$

$$Na_2CO_3 + CaSO_4 = CaCO_3 + Na_2SO_4.$$

Similar reactions take place with the salts of magnesium.

Potassium carbonate and hydroxide are similar in action and efficiency to the corresponding sodium salts. They are, however, much more expensive hence are rarely used.

A number of the salts of barium have been tried as boiler compounds. Barium chloride is the best known and least expensive of these. It effects a very satisfactory removal of sulphates according to the reaction:

$$BaCl_2 + CaSO_4 = BaSO_4 + CaCl_2.$$

It has practically no effect on the carbonates in solution. Another objection to its use is the formation of $MgCl_2$ with $MgSO_4$. This salt, as has been pointed out, has a decided corrosive effect. It is, then, a satisfactory, although rather expensive, method of removing $CaCO_3$ but is valueless in the treatment of other salts.**

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*H. de la Coux. L'eau dans l'industrie. 1900. 70.

**H. de la Coux. L'eau dans l'industrie. 1900. 70.

Barium hydroxide* gives two series of reactions in the boiler. (1) $Ca(HCO_3)_2 + Ba(OH)_2 = CaCO_3 + BaCO_3 + 2\ H_2O$.

$CaSO_4 + BaCO_3 = BaSO_4 + CaCO_3$.

These reactions take place very slowly as the $BaCO_3$ formed is only slightly soluble.

(2) $Ba(OH)_2 + CaSO_4 = BaSO_4 + Ca(OH)_2$.

$Ca(OH)_2 + Ca(HCO_3)_2 = 2\ CaCO_3 + 2\ H_2O$.

In some places it is the practice to use a mixture of $BaCl_2$ and $Ba(OH)_2$.

The value of these salts of barium is questionable. The precipitation of calcium as calcium carbonate is of doubtful value while the use of $BaCl_2$ with water containing magnesium salts is positively injurious. The low solubility of $Ba(OH)_2$ (3 parts in 100 at 0°) makes its value in a boiler questionable. In general the high price of barium salts and their doubtful value limit their use.

W. H. Booth**has this to say regarding the use of barium aluminate; "M. Taveau strongly recommends aluminate of barium, which has the disadvantage of high price enhanced by the high atomic weight of barium, viz., 137 against calcium 40. By its

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* H. de la Coux. L'eau dans l'industrie. 1900. 71.

**Water Softening and Treatment. 1911. 98.

use new deposits are rendered quite pulverulent and old scale disintegrated. He does not profess to explain the reactions, for theory does not explain the results which demand a quantity of the reagent far superior to the quantities employed successfully.

He suggests that the reagent becomes successively regenerated, and is able to act again and again much as carbonate of soda acts on carbonate of lime.

Aluminate of barium of 5° Baumé solution is advised to be used in doses proportionate to the degrees of hardness and generally about 10 grammes of the solution per degree of hardness per cubic meter of feed water. With a notable proportion of lime sulphate, $n = (3/4\ A + B)$, where A is the total hardness in degrees, B is the permanent hardness, and n is the quantity of solution in grammes per cubic meter."

Mr. Booth's point, regarding the increased amount of barium salt, which must be added to soften a given amount applies, with equal force, to the other salts of barium which we have considered.

Trisodium phosphate, Na_3PO_4, gives a very desirable precipitate of calcium phosphate. This forms as a slushy mud which may easily be blown from the boiler. Like the salts of barium its price at present is too high for general use.

A similar precipitate is obtained with the fluorides of

sodium and potassium.* Their prices are also prohibitive.

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*Albert A. Cary. The Use of Boiler Compounds. Am. Mechinist. XXII. 1902. 1154.

Sodium silicate (water glass) is recognized as a useful aid in preventing incrustation. With calcium bicarbonate a white gelatinous precipitate of calcium silicate is formed;

$$Na_2SiO_3 + Ca(HCO_3)_2 = CaSiO_3 + CO_2 + Na_2CO_3.$$

The sodium carbonate formed by this reaction may react further with more calcium bicarbonate. Sulphates are removed according to the equation;

$$Na_2SiO_3 + MgSO_4 = MgSiO_3 + Na_2SO_4.$$

In using this the amount of sulphates must be taken into consideration in calculating charges, since there is no regenerative process where a sulphate is treated. Most sodium silicates contain an excess of silicic acid over the formula Na_2SiO_3. This excess must also be taken into account in making calculations.**

**H. de la Coux. L'eau dans l'industrie. 1900. 69.

Ground glass and talc ($H_2Mg_3(SiO_3)_4$) are sometimes employed, and may have a similar action to the alkaline silicates although considered inert by many.***

***W. H. Booth. Water Softening and treatment. 1911, 99.

Chromates are also used in the boiler. Both normal and dichromate may be used but the normal is preferred on account of its lower molecular weight. The reactions involved are;

$$K_2CrO_4 + Ca(HCO_3)_2 = CaCrO_4 + K_2CO_3 + CO_2 + H_2O.$$

$$K_2CrO_4 + CaSO_4 = K_2SO_4 + CaCrO_4.$$

Again, in the case of the bicarbonate, we have K_2CO_3 as a product. This reacts further to soften another molecule of bicarbonate.* When the dichromate is used with a water having caustic alkalinity there is a reduction to the normal chromate according to the reaction;

$$K_2Cr_2O_7 + 2\ KOH = 2\ K_2CrO_4 + H_2O.$$

Other salts which are found in boiler compounds are sodium chloride, ammonium chloride, sodium sulphate and calcium sulphate. The ammonium chloride may have some action, beneficial or otherwise, due to decomposition into NH_3 and HCl. The others have no action in the boiler and are added for the sole purpose of increasing the weight and bulk of the boiler compound. Calcium sulphate, in fact, is one of the worst of scale forming minerals and when added would increase scale formation.

Plates of zinc** suspended in the boiler have been

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*H. de la Coux. L'eau dans l'industrie. 1911, 72.

**W. W. Christie. Boiler Waters. 1906. 137.

advocated for use in preventing scale formation in sulphate waters low in carbonates. The theory advocated for this action is: "That the two metals, iron and zinc, surrounded by water at a high temperature form a voltaic pile with a single liquid, which slowly decomposes the water. The liberated oxygen combines with the most oxidizable metal, the zinc, and its hydrogen equivalent is disengaged at the surface of the iron. There is thus generated over the whole extent of the iron influenced a very feeble but continuous current of hydrogen, and the bubbles of this gas isolate at each instant the metallic surface from the scale forming substance. If there is but a little of the latter, it is penetrated by these bubbles and reduced to mud; if there is more, coherent scale is produced, which being kept off by the intervening stratum of hydrogen, takes the form of the iron surface without adhering to it."

Zinc also has a beneficial action by removing the dissolved oxygen from the water thus reducing corrosion.

$$2\ Zu + O_2 = 2\ Zu\ O.$$

A novel device for preventing boiler incrustation has been worked out by Sir Wm. Armstrong at Elmswick, Newcastle-on-Tyne, Northumberland.* He demonstrated that, in generating steam, there

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*Stephen Rickard. Electricity and Boiler Incrustation. The Chemical Engineer. V. 1906, 239.

[illegible]

[illegible]

[illegible]

[illegible]

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[illegible]

is also generated a current of electricity passing from the water to the boiler plates and assisting deposition of scale. He showed this by insulating a small boiler on glass and obtaining sparks from the top.

He then used Leclanche and Daniels' cells to set up an opposing current of greater strength. Daniels' cells were found to be more effective. Several of these may be attached to a boiler at one time if desired. The water connection was made by an insulated iron rod passing through the boiler shell and terminating in a curved bell situated near a flue.

Before being used, the action upon the boiler by these currents and those set up by the zinc should be considered. The writer is inclined to be very sceptical as regards the efficiency of either method.

Painting the inside of the boiler with various things has been advocated. Painting with a thin wash of Portland cement will protect against corrosion.* M. Taveau** states that the adherence of scale may be prevented if the interior of the boiler is painted with a mixture of 25 per cent graphite and 75 per cent black mineral varnish. That such paints would combat corrosion is obvious, that they would hinder scale formation is yet to be proven.

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*W. M. Booth. Boiler Waters and their Treatment.Chem.Eng.Vol. I, 1904,366.
**W. H. Booth, Water Softening and Treatment. 1911. 99.

Graphite and various oils form another class of substances. The action of graphite is explained in this manner.*

"A very small quantity of graphite used for boilers will prevent scaling, and if the boiler already has scale on it will not only prevent further decomposition, but the minute particles will penetrate the scale and soften it so that it will drop to the bottom and can be taken out inexpensively. This assertation is based on facts. Having used water taken from the mine, which was only slightly discolored by graphite, the softening of the scale was accidently discovered. The water apparently contained nothing else which could have produced the same effect. The water was used probably two months before the discovery was made."

Petroleum is credited with a similar softening or rotting action on the scale formed. The use of the lighter volatile oils should be avoided since they may be vaporized and carried into the cylinder and other parts of the engine. There is one case on record where a boiler compound was detected a thousand feet from the boiler.** A heavy gummy oil should also be avoided as it may dry down to form a hard mass instead of the spongy precipitate

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*Fritz Cirkel. M. E. Graphite, its Properties, Occurrence, Refining and Uses. Canadian Dept. of Interior. Mines Branch. 1907. 286.

** R. S. Wallace. Boiler Compounds. Am. Mechanist. XXII,1902,1162.

desired. In general all animal and vegetable oils should be avoided and only a high grade mineral oil, which has been refined, used. Such oils have given excellent service in some cases and are well recommended by some users.*

Potters clay** has been proposed for use in the boiler. Its action is entirely mechanical and there is danger of deposits forming upon the boiler shell which will cause overheating. It is probably not as effective as ground glass and talc which have some chemical action also.

Potatoes and other starchy matter are often used in the boiler. The theory assumes that the particles of alkaline earth salts act as nuclei around which the starchy matter collects. This causes precipitation without incrustation. The addition of such substances may result in the fouling of valves, etc. That they have a beneficial action is not to be denied; that they also become a nuisance is also an assured fact. Their use is gradually being abandoned.

Fats, rosins, tallow and some gums have been tried as

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*W. H. Wakeman. The Use of Boiler Compounds. Am. Mechanist, XXII. 1902. 1014.

**H. de la Coux. L'eau dans l'industrie. 1900. 58.

boiler compounds with little or no success.*

Glycerine** when used in a boiler holds the calcium salts in solution until a high concentration is obtained. Precipitation then takes place in the form of a gelatinous mass which prevents crystallization and adherence.

The use of sugar and molasses*** also depends upon the solubility of lime in the presence of sweet matter. If rather concentrated, such a solution will hinder deposition and redissolve scale. A compound $C_{12}H_{22}O_{11}$ CaO is formed which is very soluble in water. When boiled in the generator the monocalcium sucrate changes to the sesqui and tricalcium salts having the formulae 2 $C_{12}H_{22}O_{11}$ (3CaO) and $C_{12}H_{22}O_{11}$(3CaO). The tricalcium sucrate, being the least soluble, is the one precipitated. Precipitation takes place in the form of a white mass.

When sugar is subjected to prolonged boiling it undergoes a series of changes, going to glucose, then to uncrystallizable sugar, then to ulmin and finally to ulminic acid.° It is

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*H. de la Coux. L'eau dans l'industrie. 1910. 59.

**H. de la Coux. L'eau dans l'industrie. 1910. 66.

***H. de la Coux. L'eau dans l'industrie. 1900. 65.

°U. S. Dispensatory. 19th Ed. 1907. 1075.

needless to say that any acid or acid producing substance should be barred from the boiler.

The theoretical amount necessary to soften a water has not always been the amount of compound found most effective. In many cases there is a partial regenerative reaction and the theory has called for an excess of compound. On the other hand W. M. Booth* advocates the use of more than theoretical amounts of soda ash because a scale may form around the particles. Actual experiments, with the calculated amount as a guide, are then necessary to determinethe most effective amount of compound.

The method of adding a compound is of great importance. Its addition as a concentrated solution will result in corrosion of valves and fittings while the addition of large amounts at one time will result in foaming and similar evils. A very satisfactory method of addition is described by W. M. Booth.** "A small tank holding five to ten gallons of water is connected to the suction side of the feed pump and the liquor added. The vessel is then filled with water. The cock is turned so as to allow the chemical to flow drop by drop into the water. A small guage glass aids in watching this. The reaction at once takes place and the boiler guage glass shows the sediment which is largely composed of

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*Boiler Waters and their Treatment. Chem. Engr. V, 1907, 337.

**Boiler Waters and their Treatment. Chem. Engr. III, 1905, 363.

organic matter and mineral carbonates. These rise to the surface during the boiling of the water." Such a method of addition would remove the foam producing conditions.

The materials which are used in the preparation of boiler compounds may be divided into three classes, the essential constituents of a compound, the accidental impurities introduced by the use of impure materials, and the adulterants. In such a classification the materials which we have discussed may be divided as follows:

Essentials -- Graphite, petroleum, zinc, talc(?), starch, glycerine, sugar, tannin, sodium tannate, barium hydroxide, barium chloride, barium carbonate, barium aluminate, sodium oxalate, sodium hydroxide, sodium carbonate, sodium silicate, sodium chromate, sodium dichromate, trisodium phosphate, sodium fluoride, potassium oxalate, potassium hydroxide, potassium fluoride, potassium chromate, and potassium dichromate.

Accidental impurities -- Bark, sawdust, blocks of wood, calcium and magnesium salts, sodium chloride, and silicious matter.

Adulterants -- Coal, potter's clay, fats, tallow, sodium sulphate, sodium chloride, many alkaloids and dyes of unknown composition.

CHAPTER II.

ANALYSIS OF BOILER COMPOUNDS.

As the analysis of the various compounds was carried on, a system of analysis applicable to boiler compounds was devised. The majority of the methods given have been tried on actual compounds while standard methods have been followed wherever possible. The analytical scheme is not complete and will require modification to take in things which may later be found in boiler compounds.

At present the following things are reported as being used in boiler treatment: graphite, coal, petroleum, zinc (plates), potter's clay, fats, tallow, bark, sawdust, blocks of wood, talc, starch, gums, glycerine, sugar, tannin, sodium tannate, barium hydroxide, barium chloride, barium carbonate, barium aluminate, calcium sulphate, sodium sulphate, sodium oxalate, sodium hydroxide, sodium carbonate, sodium silicate, sodium chromate, sodium dichromate, sodium chloride, trisodium phosphate, sodium fluoride, potassium oxalate, potassium hydroxide, potassium fluoride, potassium chromate, potassium dichromate, and ammonium chloride, as well as various dyes of unknown composition.

In the analytical scheme it seems desirable to precede the chemical analysis by a thorough physical examination. This physical examination consists of two parts, a gross and a

microscopic examination. Similarly the chemical analysis divides itself into two parts on the basis of the solubility of the constituents of the compound in water. The method of attack is then as follows:

Gross physical examination. -- Remove zinc plates, blocks of wood and note presence of fine glass, coal dust, greasy feeling, color and other physical properties. Materials like graphite and talc may be recognized by their color, hardness, feeling, etc. Fats and oils may also be recognized. Anything removed should be dried and weighed.

Microscopic examination. -- Bark should be identified by its brown color and fibrous structure, sawdust by its structure, more regular than ground bark. Particles of coal dust, sand and the amount of crystalline matter should be noted. If 1 per cent of any of these substances is present a careful examination should result in its identification.

Determination of water. -- Dry over night in the oven at 180° exactly 1 gram of the original compound, using a Rose crucible if graphite is suspected of being present. Loss of weight is considered to be water. In some cases charring takes place. In that case dry at 105° to constant weight.

Determination of volatile matter. -- After determining the amount of water, ignite the residue in a blast lamp for one hour. Care must be used not to burn the organic matter too rapidly causing mechanical loss of ash. Cool in a dessicator

and weigh. Loss of weight is organic matter, volatile inorganic matter, and some water of crystallization.

Determination of ash. -- The residue from the determination of volatile matter is reported as ash.

Determination of graphite. -- Ignite the ash in a slow current of oxygen. Loss of weight may be reported as graphite if previous ignition has been complete. In the case of amounts of graphite under 5 per cent, ignition to determine the graphite present should be made on a part of the insoluble portion which will contain a larger proportion of graphite.

Petroleum ether extract. -- Extract a 1 gram sample of the original compound with petroleum either for 16 hours in a Soxhlet extractor. Dry on a water bath and cool in a dessicator. Weigh the residue as ether extract or weigh the substance before and after extraction and take the difference to be ether extract. This determination is accurate to about .5 per cent. The extracted matter contains fats and petroleum oils. These may be distinguished by treatment with concentrated H_2SO_4 which does not attack petroleum.

Division into soluble and insoluble portions and preparation of solution for analysis. -- Add to a 10 gram sample 200 cc. of distilled water. Shake thoroughly and allow time for solution. If not completely dissolved filter off the insoluble portion or, if a liquid, separate with a separatory funnel. Make

up the soluble portion to 1 liter with distilled water.

Insoluble Portion.

The insoluble portion may contain barium carbonate, calcium sulphate, graphite, coal petroleum, ground glass, potter's clay, fats, tallow, bark, sawdust, talc, or starch.

Determination of sulphates and of barium.-- Acidify an aliquot portion of the insoluble matter with HCl and boil for 15 minutes. Any gas evolved is probably CO_2. Confirm by precipitation of $CaCO_3$ from lime water. Allow time for complete solution, filter and make up to 100 cc. with distilled water. Divide into two 50 cc. portions. To one add an excess of dilute H_2SO_4 precipitating barium (from $BaCO_3$ and $Ba(OH)_2$). To the second portion add an excess of $BaCl_2$ (10 per cent solution) precipitating SO_4 (from $CaSO_4$). Both of the precipitations should be made by adding the reagent slowly to the hot solution with constant stirring. The precipitate should be filtered off, ignited and weighed. These determinations are reliable to .2 per cent. (This determination will also include any barium present in clay or talc.)

Detection of clay, talc and calcium. -- Boil a small portion of the insoluble matter in HCl for 15 minutes. Add an excess of NH_4OH. A white gelatinous precipitate is $Al(OH)_3$ (from potter's clay). Add $(NH_4)_2\ CO_3$. A white precipitate

is $CaCO_3$. Add Na_2CO_3 in excess precipitating magnesium (from talc) if present. Tests are accurate to 1 per cent.

Estimation of calcium. -- Dissolve an aliquot portion of the insoluble matter in hot HCl. Add to the hot solution ammonium oxalate, drop by drop, until precipitation is complete. Filter and ignite the precipitate to CaO. (This also may include any calcium present in talc or clay.) The determination is accurate to .2 per cent.

Determination of insoluble starch. -- Crush a small portion of the insoluble matter, extract thoroughly with water and add a drop of solution of iodine in KI. If starch is present, an intense blue color will be formed. Accurate to .01 per cent.

Stir an aliquot portion of the insoluble portion (representing from 2.5 to 3 grams of the dry material) in a beaker with 50 cc. of water for one hour. Transfer to a filter and wash with 250 cc. of water. Heat the insoluble residue for 2 1/2 hours with 200 cc. of water and 20 cc. HCl (Sp.gr. 1.125) in a flask provided with a reflux condenser. Cool, and nearly neutralize with sodium hydroxide. Complete the volume to 250 cc., filter and determine the dextrose in an aliquot portion.* The weight of dextrose multiplied by .90 gives the weight of starch.**

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*Water Soluble Portion. Detection and estimation of reducing sugars.

**Official and Provisional Methods of Analysis. Bull. #107. Bureau of Chemistry, Dept. of Agriculture, 1907, 53.

Water Soluble Portion.

May contain potassium, sodium, barium, and ammonium as oxalates, hydroxides, chlorides, aluminates, phosphates, fluorides, silicates, chromates, dichromates, tannates, or sulphates and soluble starch, gums, glycerine, sugars or tannins.

1. Alkalinity. -- Alkalinity may be due to OH, CO_3 or PO_4 ions. Titrate a 25 cc. sample of the solution with N/50 H_2SO_4 using (1) phenolphthalein and (2) methyl orange as indicators. Care should be used to have the solution cold and to shake as little necessary while determining the phenolphthalein alkalinity. If a gelatinous white precipitate be obtained during titration it indicates SiO_2 from sodium silicate. The titration is accurate to .5 per cent.

Determination of PO_4. -- Acidify a fresh portion (50 cc.) of solution with HNO_3 and add ammonium molybdate to the hot solution until precipitation is complete. A yellow precipitate indicates phosphate. Digest at about 65°C. for an hour on the water bath and add more molybdate solution. Filter and dissolve the precipitate on the filter with NH_4OH and hot water. Nearly neutralize with HCl, cool, acidify and add magnesia mixture from a burette. Add slowly with constant stirring. After 15 minutes add 12 cc. of NH_4OH, specific gravity 0.90. Let stand for 2 hours, filter and weigh. Calculate to PO_4. Accurate to .2 per cent.*

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*Official and Provisional Methods of Analysis. Bull. 107. Bureau of Chemistry, Dept. of Agriculture, 3.

Calculation of OH and CO_3 alkalinity. -- Subtract the phenolphthalein alkalinity from the methyl orange alkalinity and multiply the difference by 2 giving the carbonate alkalinity as $CaCO_3$. (x 1.06 = Na_2CO_3). Calculate the phosphate alkalinity as $CaCO_3$. From the methyl orange alkalinity subtract the sum of the carbonate and phosphate alkalinities. (as $CaCO_3$). The difference is caustic alkalinity. (x .80 = NaOH).

2. Determination of Cl. -- To a fresh portion (25 cc.) add 1 cc. of 5 per cent K_2CrO_4 solution. Titrate with standard $AgNO_3$ solution (1 cc. = .5 MgCl) until a red color, Ag_2CrO_4, begins to appear. Subtract .2 cc. for the indicator. Calculate to Cl. Accurate to .5 per cent.

3. Determination of SO_4. -- Acidify a fresh portion (50 cc.) with HCl and heat to boiling. Add $BaCl_2$ slowly with constant stirring until precipitation is complete. Filter and ignite. Calculate to SO_4. Accurate to .2 per cent.

4. Determination of silica, sodium and potassium. -- Acidify 100 cc. of the solution with HCl and evaporate to dryness on the water bath in a platinum dish. Dissolve the residue in hot water, add HCl and filter. Again evaporate to dryness, take up with water and filter as before combining the two precipitates. Ignite and weigh as SiO_2. If the solution contained sulphates remove by precipitating with alkali free barium chloride and filtering.

"The filtrate contains sodium and potassium. Evaporate

to dryness, add hot water and a saturated solution of barium hydroxide free from alkalies until a slight film collects on top of the solution. Filter, wash with hot water, add to the filtrate an excess of ammonium carbonate. Filter. Evaporate the filtrate to dryness. Dry and ignite at a low red heat to expel ammonium salts. Repeat the operation (from the addition of $Ba(OH)_2$) until no further precipitate is obtained by $Ba(OH)_2$ or $(NH_4)_2 CO_3$. Evaporate to dryness in a weighed platinum dish and weigh the chlorides of sodium and potassium. Add 25 cc. of water and a few drops of hydrochloric acid and add 1 cc. of a 10 per cent platinic chloride solution for each 30 mg. of the combined chlorides. Evaporate to dryness in a platinum dish on a plate over the water bath. Wash with 80 per cent alcohol until the liquid is no longer colored. Dry and dissolve the precipitate in the dish and on the filter in hot water. Evaporate to dryness and weigh as K_2PtCl_6.

$$K_2PtCl_6 \times .161 = K.$$

$$K_2PtCl_6 \times .307 = KCl.$$

Subtract weight of KCl from combined KCl and NaCl.

$$NaCl \times .394 = Na."*$$

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*Notes on Water Analysis. Ch. 3, 4.

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5. Determination of tannin. -- Add $FeCl_3$ solution to a few cc. of the solution. Blue or green color indicates tannin or sodium tannate if solution was alkaline. If tannin is present

determine as follows:

Total soluble. "Filter and evaporate to dryness an aliquot portion of solution in a weighed platinum dish (100 cc. is a convenient quantity). Dry at 105°C. and weigh.

Non tannins. Prepare a sufficient quantity of hide powder in the following manner. Digest with 25 times its weight of water until thoroughly soaked; add 3 per cent of chrome alum in solution, agitate occasionally for several hours, and allow to stand over night. Wash, by squeezing through linen, until the water gives no precipitate with $BaCl_2$. Squeeze the hide, using a press if necessary, so that it contains 70 to 75 per cent water and determine the moisture. (5 grams is a convenient quantity).

Add to 200 cc. of the tannin solution such a quantity of the wet hide as contains 12 to 13 grams of dry hide, shake for 10 minutes and squeeze through linen." Filter and dry 100 cc. Correct the weight of the residue for the water contained in the wet hide.

Tannins. The difference between total solids and non tannins is the weight of tannin in 100 cc. of solution.* This method of determining tannin is accurate to 2 per cent.

6. Determination of Volatile Acids. -- To 100 cc. of solution add H_2SO_4 until strongly acid. Distill in steam as long as the distillate is acid to litmus. Make up to 100 cc. and

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*Official and Provisional Methods of Analysis. Bull. 107. Bureau of Chemistry, Dept. of Agriculture. 36.

titrate an aliquot portion with N/50 NaOH using phenolphthalein as an indicator. Calculate as acetic acid unless proven to be a higher acid. Accurate to 1 per cent.

7. Determination of Oxalates. -- Make a fresh portion of the solution (50 cc.) alkaline with NH_4OH. Heat to boiling and add a saturated solution of $CaSO_4$ to the boiling solution. Stir vigorously. Allow the precipitate to settle, filter, ignite to CaO and weigh. Calculate to C_2O_4. Accurate to .2 per cent.

8. Determination of chromates and of aluminium. -- To another small portion add $(NH_4)_2S$. Precipitate Al and Cr (from chromates and dichromates). Dissolve the precipitate in HNO_3, add $KClO_3$ crystals and concentrate.

Dilute a portion of the solution, add NH_4OH in excess, acidify with acetic acid and add lead acetate. Precipitate yellow $PbCrO_4$ if chromium is present.	Boil another portion with NaOH, dilute and filter. Filtrate $NaAlO_2$. Acidify with HCl and add $(NH_4)_2CO_3$. Precipitate $Al(OH)_3$.

If Al is present add to 50 cc. of the original solution 5 cc. of HCl. Add dilute NH_4OH in slight excess. Boil for a few minutes and filter. Dissolve in HNO_3 and precipitate as before. Filter, ignite and weigh as Al_2O_3. Accurate to .2 per cent.*

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*C. W. Foulk. Notes on Quantitative Chemical Analysis. 1910. 149.

If chromates are present make a fresh portion (50 cc.) weakly acid with acetic acid. Heat to boiling and add barium acetate drop by drop with constant stirring. Allow to stand and filter through a Gooch crucible (without using strong suction as otherwise the filter will clog). Wash with dilute alcohol and dry in the oven. Heat, covered with a large crucible, for five minutes in the flame of a Bunsen burner. Remove cover and ignite to a uniform yellow color.*

9. Determination of Ba. -- Heat 50 cc. of the original solution, add dilute H_2SO_4 until precipitation is complete. Let stand for 30 minutes, filter, ignite and weigh. Calculate to Ba. Correct to .2 per cent.

10. Determination of NH_3. -- To a small portion of the original solution add strong NaOH and warm. NH_3 is evolved, recognized by its odor and the formation of NH_4Cl fumes with HCl. If enough ammonia is present to give this test, take a 25 cc. sample of the solution, make up to 500 cc. with NH_3 free water and add 5 cc. of saturated sodium carbonate solution. Distill off 200 cc. into a graduated flask and nesslerize an aliquot portion or distill into an excess of standard acid if ammonia content is too high for nesslerization. Note amount of acid neutralized.

11. Determination of glycerine. -- Concentrate an

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*Treadwell and Hall. Analytical Chemistry. 3rd Ed. II. 104.

aliquot portion of solution until it does not contain over 60 per cent of water.*

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*Sherman. Organic Analysis. 276.

In a narrow-mouthed flask, which has been thoroughly cleaned and dried, weigh 1.25 to 1.5 grams of sample. Add about 3 grams of anhydrous solium acetate, then 7.5 cc. of acetic anhydride. Connect with an upright Liebig condenser. For convenience the inner tube should not be over 50 cm. long and 9 - 10 mm. inside diameter. Use a ground glass stopped (preferably) or a rubber one. If a rubber stopper is used it must be treated with hot acetic anhydride vapor before using. Keep just at boiling for 1 hour preventing the salts from drying on the inside of the flask. Allow the mixture to cool somewhat then add 50 cc. of distilled water (temperature 80°) through the condenser. (This would best be added before the contents solidify although if necessary it may be left over night.)

Cool the solution without removing the condenser then wash the condenser and stopper into the flask. Filter through an acid-washed filter into a 1 liter flask of Jena glass. Wash with cold, CO_2 free water. Add 2 cc. phenolphthalein solution and titrate with NaOH until a pink color appears. Now run in 50 cc. of normal NaOH. Boil gently for 15 minutes using a glass tube as an air condenser. Cool quickly as possible and titrate with normal acid.

From the per cent of NaOH consumed, calculate the per cent glycerol (including acetylizable impurities) after making corrections for the blank.

1 cc. normal NaOH = .03069 grams glycerol.

Coefficient of expansion for normal solutions is .00033 per cc. per degree. Apply this correction if necessary. Accurate to .5 per cent.

Blank.

Make a blank test using the same amount of acetate, anhydride and water as in the determination. The same procedure should be followed except that filtration is not necessary and not more than 10 cc. of the NaOH solution need be added.

12. Estimation of sugars and starch.*

Preparation of Fehling's solution.

a. Copper sulphate solution. Dissolve 34.639 grams of $CuSO_4,5\ H_2O$ in water and dilute to 500 cc.

b. Alkaline tartrate solution. Dissolve 173 grams of Rochelle salts and 50 grams of NaOH in water and dilute to 500 cc.

c. Mixed solution. Mix equal volumes of (a) and (b) immediately before using.

Determination of reducing sugars.

Boil 50 cc. of solution and add 25 cc. of Fehling's

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*Official and Provisional Methods of Analysis. Bull. 107. Bureau of Chemistry, Dept. of Agriculture. 39-56.

solution to the briskly boiling solution. Continue to boil for four minutes. Filter through asbestos, in a Gooch crucible, which has been washed with hot water, alcohol and ether, and then dried at 100°C. Wash precipitate with hot water, then with 10 cc. of alcohol, then with 10 cc. of ether. Dry 30 minutes in a water oven; cool and weigh as cuprous oxide. Or ignite the precipitate in an open crucible and weigh as cupric oxide. Calculate as dextrose. Allihn's table for the determination of dextrose.*

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*Official and Provisional Methods of Analysis. Bull. 107. Bureau of Chemistry, Dept. of Agriculture. 50-51.)

Determination of sucrose.

To a fresh portion (50 cc.) of the solution add 25 cc. of water and place in a 100 cc. flask. Then add, little by little, while rotating the flask, 5 cc. of hydrochloric acid containing 38.8 per cent acid. After mixing, place in a water bath heated to 70°. (The solution comes to an even temperature in from 2 to 3 minutes.) Maintain the temperature as near 69° as is possible during 7 to 7 1/2 minutes, making a total time of heating of 10 minutes. Remove the flask, cool, exactly neutralize the acid and determine the reducing sugars. The difference between the amount of reducing sugars before and after hydrolysis multiplied by .95 gives the weight of sucrose. The solution should be clarified

Allihn's table for the determination of dextrose.

Mgs. of Copper	Mgs. of Dextrose	Mgs. of Copper	Mgs. of Dextrose
15	8.6	240	123.9
20	11.0	245	126.6
25	13.5	250	129.2
30	16.0	255	131.9
35	18.5	260	134.6
40	20.9	265	137.3
45	23.4	270	140.0
50	25.9	275	142.8
55	28.4	280	145.5
60	30.8	285	148.3
65	33.3	290	151.0
70	35.8	295	153.8
75	38.3	300	156.5
80	40.8	305	159.3
85	43.4	310	162.0
90	45.9	315	164.8
95	48.4	320	167.5
100	50.9	325	170.3
105	53.5	330	173.1
110	56.0	335	175.9
115	58.6	340	178.7
120	61.1	345	181.5
125	63.7	350	184.3
130	66.2	355	187.2
135	68.8	360	190.0
140	71.3	365	192.9
145	73.9	370	195.7
150	76.5	375	198.6
155	79.1	380	201.4
160	81.7	385	204.3
165	84.3	390	207.1
170	86.9	395	210.0
175	89.5	400	212.9
180	92.1	405	215.8
185	94.7	410	218.7
190	97.3	415	221.6
195	100.0	420	224.5
200	102.6	425	227.5
205	105.3	430	230.4
210	107.9	435	233.4
215	110.6	440	236.3
220	113.2	445	239.3
225	115.9	450	242.2
230	118.5	455	245.2
235	121.2	460	248.1

with normal lead acetate and the excess of lead removed before the determinations. Accurate to .5 per cent.

Determination of soluble starch.

Hydrolyze a fresh portion (50 cc.) in the manner given for starch under "Insoluble portion". Determine the reducing sugar formed and subtract from this value the amount of reducing sugars determined under sucrose. The difference multiplied by .90 = amount of starch.

Optical methods.

Optical methods of determining carbohydrates are very accurate and may be applied bo boiler compound analysis unless the nature of the compound makes its clarification too difficult.

Preparation of reagents.

Lead subacetate solution. -- Prepare by boiling 430 grams of normal lead acetate, 130 grams of litharge, and 1000 cc. of water for half an hour. Allow the mixture to cool and settle and dilute the supernatant liquid to 1.25 specific gravity with recently boiled water. Solid lead subacetate may be substituted for the normal salt and litharge in the preparation of the solution.

Alumina cream. -- Prepare a cold saturated solution of alum in water and divide into two unequal portions. Add a slight excess of ammonium hydroxide to the larger portion then add by

degrees the remaining alum solution until a faintly acid solution is secured.

Taking of rotations.

Rotations should be taken at 20°C. Clarify 50 cc. of the original solution with lead subacetate and take the rotation. Invert the solution in the manner described under "Determination of sucrose". If necessary, again clarify and take the rotation of the inverted sugar. Calculate the percent of sucrose present from the formula: $S = \dfrac{100\ (P - I)}{142.66 - \frac{T}{2}}$

s = per cent of sucrose
P = direct reading
I = invert reading
T = temperature at which readings are made.

Then calculate the total amount of sugars present from the rotation of the inverted solution and from this data the amounts of invert sugar and sucrose present. This determination cannot be used in the presence of dextrose but dextrose alone may be estimated by taking the rotation of the solution.

Dextrose $a_D = 52^{\circ}.8$

Sucrose $a_D = 66^{\circ}.5$

Invert sugar $a_D = -37^{\circ}.4$

CHAPTER III.

ANALYTICAL RESULTS.

Ten compounds, collected from various users of boiler compounds, were analyzed by the methods outlined. Tests were made for all things spoken of in the outline except sodium and potassium. No evidence was found of the presence of potassium in any compound so sodium was not determined, but all ions were calculated to their sodium salts.

With the results of each analysis will be given a short discussion of the compound. This will take up its softening powers and its commercial value.

Compound No. 1. -- This compound is a white, finely divided, odorless salt which does not cake. The analysis gave the following results:

Water	26.0 per cent
Organic or Volatile	6.0
SiO_2	1.1
Cl	3.0
PO_4	32.3
Mg	1.6
Ca	.9
Phenolphthalein Alkalinity (as $CaCO_3$)	21.4
M. O. Alkalinity (as $CaCO_3$)	57.4

PO_4 Alkalinity (as $CaCO_3$)	51.0
Ca Alkalinity (as $CaCO_3$)	2.2
Mg Alkalinity (as $CaCO_3$)	4.8

Hence no OH or CO_3 alkalinity.

Substances probably present.

Water	26.0
Organic or Volatile	6.0
$CaCO_3$	2.2
$MgCO_3$	4.0
Na_3PO_4	55.8
NaCl	5.0
SiO_2	1.1

This compound contains a rather high percent of calcium and magnesium carbonates, which are scale forming minerals. This would reduce the effectiveness of the phosphate to a point where 50 per cent of the compound would react with the scale. Sodium phosphate, 68 per cent pure, is quoted at $3.00 - $3.25 per hundred, f.o.b. Tampa.* This would show the compound to be worth about 4 cents per pound since the other constituents seem to be natural impurities.

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*Oil, paint and drug reporter. Vol. 87, No. 19. 1915.

Compound No. 2. -- This compound is a white odorless powder which does not cake. The analysis showed the following results:

Water	16.1 per cent
Organic or Volatile	4.5
Ash	79.4
SiO_2	.1
Mg	2.3
Ca	.2
M.O. alkalinity	75.7
Phen. alkalinity	38.0
Mg alkalinity (as $CaCO_3$)	5.6
Ca alkalinity (as $CaCO_3$)	.5
CO_3 alkalinity	69.6

Substances probably present:

Water	16.1
Organic or volatile	4.5
SiO_2	.1
$MgCO_3$	4.7
$CaCO_3$	.5
Na_2CO_3	73.8
	99.7

This is a good sample of soda ash. It is an effective softener but will increase foaming, especially if improperly

added. 75 per cent soda ash is quoted at $.80 to $1.00 per hundred depending on the quantity bought.*

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*Oil, paint and drug reporter. Vol. 87, No. 19. 1915.

Compound No. 3. -- This compound is light brown in color. It contains many small lumps and has a slight tendency to cake. It has a faint odor which is rather pleasant. The analysis showed the following results:

Water	9.4 per cent
Organic or Volatile	10.4
Ash	80.2
SiO_2	.9
Cl	2.2
Phen. alkalinity (as $CaCO_3$)	33.3
M. O. alkalinity (as $CaCO_3$)	70.7

Substances probably present:

Water	9.4
Organic or Volatile	10.4
SiO_2	.9
NaCl	3.6
Na_2CO_3	74.9
	99.2

This compound is almost identical with No. 2 in action. It differs from it only in the fact that it has a small amount of

colored organic matter probably added to disguise its composition. Its cost is also about $1.00 per hundred.

Compound No. 4. -- This compound forming a hard mass, is reddish brown in color, has a faint odor, and cakes very easily. The analysis gave the following results:

Water	20.9 per cent
Organic or Volatile	22.6
Ash	57.5
SiO_2	.5
Cl	1.0
Mg	.6
SO_4	18.4
Phen. alkalinity (as $CaCO_3$)	13.5
M. O. alkalinity (as $CaCO_3$)	26.4
Mg alkalinity (as $CaCO_3$)	2.3
CO_3 alkalinity	24.1

Substances probably present:

Water	20.9
Organic and Volatile	22.6
SiO_2	.5
NaCl	1.8
Na_2SO_4	26.7
$MgCO_3$	2.0
Na_2CO_3	25.6
	100.1

This is a very poor specimen of a boiler compound. The Na_2CO_3 is the only effective agent. It forms but one-fourth of the whole compound, the rest being useless. The Na_2SO_4 is valueless as a softening agent. The additional amount of sodium salt introduced into the boiler would also tend to increase foaming. There is no motive for adding the Na_2SO_4 to the compound except to increase its weight.

Na_2SO_4 can be purchased at 60 - 75 cents* per hundred while soda ash is but little more expensive. Such a compound can be manufactured for less than 1 cent per pound. Economical reasons alone should prohibit its use.

Compound No. 5. -- This compound is a brown liquid, very viscous which dries to a hard cement like substance when exposed to the air. It has no odor. The analysis gave the following results:

Water	43.9 per cent
Organic and Volatile	4.7
SiO_2	18.7
Cl	6.8
Phen. alkalinity (as $CaCO_3$)	24.6
M. O. alkalinity (as $CaCO_3$)	26.6

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*Oil, paint and drug reporter. LXXXVII. No. 20, p. 40.

Substances probably present:

Water	43.9
Organic and Volatile	4.7
SiO_2	18.7
Na_2O	16.3
Na_2CO_3	4.2
NaCl	11.3
	99.1

The sodium chloride and the organic matter present are adulterants. In general sodium silicate is a good softener but this is a rather poor specimen of that type of compound. Sodium silicate (Density 1.5) is quoted at \$21 - \$22 per ton.* The boiler compound runs much lower than this in density.

Compound No. 6. -- This compound is a bright blue liquid. It is slightly viscous but not gummy. It has no odor. The analysis gave the following results:

Water	56.3 per cent
Organic or Volatile	5.9
SiO_2	19.7
SO_4	1.0
Phen. alkalinity (as $CaCO_3$)	20.1
M. O. alkalinity (as $CaCO_3$)	22.9

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*The Chemical Trade Journal and Chemical Engineer. LVI, 412. 1915.

Substances probably present:

Water	56.3
Organic or Volatile	5.9
SiO_2	19.7
Na_2SO_4	1.5
Na_2CO_3	5.9
Na_2O	10.7
	100.0

This is a much better specimen of a silicate compound than No. 5. It contains no adulterants except an organic dye added to disguise the appearance of the compound. It flows easily and does not dry into a hard cake as No. 5 does. Its value is practically the same as No. 5.

Compound No. 7. -- This compound has the ordinary characteristics of powdered graphite; gray color, metallic luster, greasy feeling and flaky appearance. The analysis showed the following composition:

Water	.5 per cent
Organic or Volatile	2.6
Graphite	82.0
Silicious Matter	14.2
	99.3

This sample of graphite is slightly above the average in purity and should give good service. Its value is 7 - 8 cents

per pound.*

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*Fritz Cirkel, M. E. Graphite, its properties, occurrence, refining and uses. Canadian Dept.of Interior. Mines Branch, 1907, 156.

Compound No. 8. -- This compound is a dark brown powder with some material of a lighter color occasionally appearing in it. It is very light in weight and apparently of organic origin. Its odor resembles that of hay or of tea. Analysis showed 16 - 18 per cent of tannin present and that the compound was 58 per cent soluble in water. A qualitative analysis for the source of tannin* showed that the material was from oak bark. The per cent of tannin and of soluble matter, as well as the large amount of crystalline matter seen when examined with a microscope, indicate that the substance is a dried extract of bark rather than a crude bark.

This compound would be effective in removing scale but would tend to be corrosive. Its commercial value is about 8 cents per pound.*

Compound No. 9. -- This compound was a black tarry substance with an unpleasant odor. The analysis gave the following

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*Allen. Commercial organic analysis. V. 42.

*Chemical Trade Journal. Vol. 56, p. 390. 1915.

results:

Water	63.0 per cent
Organic or Volatile	11.7
Phen. alkalinity (as $CaCO_3$)	29.2
M. O. alkalinity (as $CaCO_3$)	30.8

Substances probably present:

Water	63.0
Organic or Volatile	11.7
NaOH	22.1
Na_2CO_3	3.4
	100.2

The organic matter contained 1 per cent of starch and was of vegetable origin. Caustic soda is quoted at$3.25 per hundred.* The sodium hydroxide present in the compound is then worth less than 1 cent per pound. The organic matter is not of uniform composition and is also doubtless of slight value.

Compound No. 10. -- This compound was similar to No. 9 in appearance and odor, but seemed to be slightly more solid. The analysis gave the following results:

Water	35.9 per cent
Organic or Volatile	29.7
Cl	.2
M. O. alkalinity (as $CaCO_3$)	32.4
Phen. alkalinity (as $CaCO_3$)	16.0

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*Oil, paint and drug reporter. Vol. 87, No. 19.

Substances probably present:

Water	35.9
Organic or Volatile	29.7
NaCl	.3
Na_2CO_3	34.3
	100.2

The organic matter in this compound, like that in No. 9 is of vegetable origin and not of constant composition. The value of the compound is probably slight. Its softening powers are similar to that of other soda ash compounds.

	I	II	III	IV	V	VI	VII	VIII	IX	X
Water	26.0	16.1	9.4	20.9	43.9	56.3	.5	97.0	63.0	35.9
Organic	6.0	4.5	10.4	22.6	4.7	5.9	2.6		11.7	29.7
M.O.alk.	57.4	75.7	70.7	26.4	26.6	22.9	---	---	30.8	32.4
Phen.alk.	21.4	38.0	33.3	13.5	24.6	20.1	---	---	29.2	16.0
Na_2CO_3	---	73.8	74.9	25.6	4.3	5.9	---	---	3.4	34.3
$MgCO_3$	4.0	4.7	---	2.0	---	---	---	---	---	---
$CaCO_3$	2.2	0.3	---	---	---	---	---	---	---	---
NaOH	---	---	---	---	21.0	13.8	---	---	22.1	---
Na_3PO_4	55.8	---	---	---	---	---	---	---	---	---
Na_2SO_4	---	---	---	26.7	---	1.5	---	----	---	---
NaCl	5.0	---	3.6	1.8	11.3	---	---	----	---	.3
SiO_2	1.1	.1	.9	.5	18.7	19.7	14.2	---	---	---
Graphite	---	---	---	---	---	---	82.0	---	---	---
Tannin	---	---	---	---	---	---	---	16.-18.	---	---
Price	.03	.01	.01	---	.02-.03	.02-.03	.07-.08	.08	.01-.02	.01-.02

CONCLUSIONS.

I. On the basis of composition the compounds analysed may be divided into the following classes:

1. Those having sodium carbonate for a base. Nos. II, III, IV, and X.
2. Those having sodium hydroxide for a base. No. IX.
3. Those having sodium silicate for a base. Nos. V and VI.
4. Those having sodium phosphate for a base. No. I.
5. Those having graphite for a base. No. VII.
6. Those having tannin for a base. No. VIII.

II. Since the softening powers of an alkaline compound depend upon the action of the sodium salts (except in the case of the relatively insoluble $Ca(OH)_2$ and $Ba(OH)_2$), the alkalinity of any such compound toward phenolphthalein and methyl orange may be taken as an index of its effectiveness.

III. Since sodium salts of similar grades to those used in boiler compounds may be bought for the following prices:

Phosphate	\$3.00 per hundred pounds,
Hydroxide	\$3.25 per hundred pounds,
Soda ash	\$0.80 - \$1.00 per hundred pounds,

and any organic substance added is probably inexpensive, the cost of materials used in preparing will vary from 1 - 4 cents per pound.

IV. Much more work may be done on boiler compounds, in perfecting means of analysis and in studying their action in the boiler.

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